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Surprising Catalytic Activity of Bismuth (III) Triflate in the Friedel-Crafts Acylation Reaction[1]

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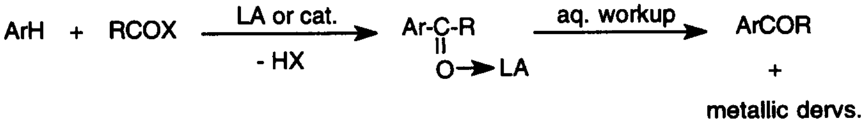
Abstract. *Bismuth tris-trifluoromethanesulfonate ($Bi(OTf)_3$) was found to be a novel catalyst for the Friedel-Crafts acylation. The reactions of activated or deactivated benzenes such as fluorobenzene proceeded in high yields in the presence of a catalytic amount of $Bi(OTf)_3$. This catalyst is water stable and its catalytic activity is much higher than the one of the other metallic triflates $M(OTf)_3$ previously reported (M = Al, Ga, Ln or Sc).* © 1997 Elsevier Science Ltd.

As a result of the complexation of the Lewis acid (LA) with the arylketone product, the Friedel-Crafts acylation (eq.1) has been as a promoted self-blocking reaction. In these reactions, the use of stoichiometric amounts of activator is required. Such is the case for the aluminum chloride[2] which is the industrially used activator. As a result, the major drawback of the Friedel-Crafts acylation in full scale plant consists of serious effluent problems. In order to develop a true catalytic cycle, two solutions seem obvious, but difficult to carry out : the catalyst must activate selectively the acylating agent (RCOX, X= Cl or OCOR), and/or must be broken of the complex by any means, for example by thermal reaction with graphite.[3]



$$\mathrm{ArH} + \mathrm{RCOX} \xrightarrow[-\,\mathrm{HX}]{\text{LA or cat.}} \mathrm{Ar}\text{-}\underset{\underset{\mathrm{O}\rightarrow\mathrm{LA}}{\|}}{\mathrm{C}}\text{-}\mathrm{R} \xrightarrow{\text{aq. workup}} \begin{array}{c}\mathrm{ArCOR}\\ +\\ \text{metallic dervs.}\end{array} \qquad (1)$$

Some catalysts, in particular iron salts as $FeCl_3$,[4,5] allow the development of a catalytic cycle, but the necessarily drastic conditions often lead to side reactions. Brönsted acids are efficient catalysts, in particular triflic acid[6] or superacidic systems,[7] but their activity is restricted to the more stable reagents or substrates as aroyl triflates.[8] The catalysts recently reported are active only for the acylation of activated aromatic substrates such as aromatic ethers, for instance Lewis acid-lithium or silver salt systems,[9] activated zinc chloride ("Clayzic"),[10] zeolites,[11] metallic chlorides,[12] transition metal triflates[13] or metal-bis(trifluoromethylsulfonyl)amides.[14] However, hafnium triflate, in presence of an excess of lithium perchlorate, leads to the acylation of benzene (17%) and of toluene (87%).[15] The catalytic activity of the boron, aluminum and gallium triflates is low since 50 mol % of these compounds gave a maximum 72% yield in the acylation of toluene[16] by acyl chlorides (MeCOCl, PhCOCl).

With regard to the research initiated in our laboratory on acylation reactions, we discovered that bismuth (III) chloride or $BiCl_3$-metallic iodide systems are the first true catalysts able to carry out the acylation of enoxysilanes[17] and allylsilanes.[18] On the other hand, $BiCl_3$ and various Bi(III) derivatives such as oxide, oxychloride, carboxylates show a very good catalytic activity for the Friedel-Crafts acylation of aromatic ethers.[19,20] A preferential complexation of the active Bi-species ($BiCl_3$) with the acylating agent (X=Cl) rather than with the ketone explains this result.[20b] Nevertheless, $BiCl_3$ and these Bi-derivatives are inefficient catalysts for the acylation of benzene, toluene, or deactivated aromatics. With the aim of achieving the catalytic acylation of these aromatic compounds, we decided to study the catalytic power of Bi-compounds bearing strongly electron-withdrawing ligands, such as polyfluoroalkane-carboxylate or -sulfonate groups.

First, we decided to carry out the acylation of an activated aromatic as anisole in the presence of 1 to 5% $Bi(OTf)_3$ (Table, entries 1-5).[21] The results obtained were better than those obtained with $BiCl_3$,[20] the reaction temperature was lower and the reaction times shorter. The reactions can be achieved either in nitromethane or in solvent-free conditions at higher temperatures.

Surprisingly, the benzoylation of aromatics such as trifluoromethoxybenzene, toluene, fluorobenzene, benzene and especially deactivated substrate as chlorobenzene has been achieved in high yields (entries 6-11) in the presence of 10% $Bi(OTf)_3$, without solvent. It is important to notice that the acylation of these aromatics was not observed in the presence of catalytic amounts of transition metal triflates (Sc, rare earths).[13] Finally, other bismuth (III) derivatives as $Bi(OCOCF_3)_3$, $Bi(OSO_2F)_3$ or $Bi(OSO_2Me)_3$, were inefficient for the same reactions.

In a typical procedure 1.16 g (1.6 mmol) of $Bi(OTf)_3.4\ H_2O$, 5.19 g (32 mmol) of trifluoromethoxybenzene and 2.25 g (16 mmmol) of benzoyl chloride were successively introduced under argon in a 50 mL flask surrounded by a condenser. The suspension was heated with an oil bath. After cooling, dichloromethane (20 mL) and water (20 mL) were added to the dark solution and the products were extracted twice with 20 mL of dichloromethane. The combined organic phases were dried ($MgSO_4$) and concentrated. The crude products were purified by flash chromatography (silica, pentane/ether 9/1) to give **7** (3.72 g, 87 %).

The study of the reaction mechanism of the noteworthy catalytic activity of bismuth (III) triflate for the Friedel-Crafts acylation is in progress.

Table. Friedel-Crafts Acylation of Aromatics Catalyzed by Bismuth Triflate

Entry	ArH[a]	RCOX	Conditions[b] T°C; time	Product[c] (*o/m/p*)	Conversion and yield[d] (%)
1	**1a**	MeCOCl	50; 2h	**4** (2 / 0 / 98)	90 (80)
2	**1a**	MeCOCl	50; 3h	**4** (2 / 0 / 98)	85 (75)
3	**1a**	$(MeCO)_2O$	50; 2h	**4** (2 / 0 / 98)	100 (96)
4	**1a**	$Me_2CHCOCl$	80; 1h	**5** (1 / 0 / 99)	100 (96)
5	**1a**	PhCOCl	110; 3h	**6** (8 / 0 / 92)	92 (81)
6	**1b**	PhCOCl	reflux; 5h	**7** (4 / 0 / 96)	98 (87)
7	**1c**	PhCOCl	reflux; 5h	**8** (19 / 2 / 79)	100 (95)
8	**1c**	$(PhCO)_2O$	reflux; 5h	**8** (19 / 2 / 79)	100 (95)
9	**1d**	PhCOCl	reflux; 5h	**9** (0 / 0 / 100)	93 (86)
10	**1e**	PhCOCl	reflux; 5h	**10**	85 (78)
11	**1f**	PhCOCl	120; 5h	**11** (13 / 0 / 87)	95 (89)

a) ArH = anisole (**1a**), trifluoromethoxybenzene (**1b**), toluene (**1c**), fluorobenzene (**1d**), benzene (**1e**), chlorobenzene (**1f**); b) ArH/RCOX = 2/1; catalyst (% towards the minor reagent: $Bi(OTf)_3$ (1% for entry 3; 5% for entries 1,2,4,5; 10% for entries 6-11); experiments have been carried out without solvent except for entries 1,3,4 (nitromethane 1M); c) All products, methoxyacetophenone (**4**), methoxyisobutyrophenone (**5**), methoxybenzophenone (**6**), trifluoromethoxybenzophenone (**7**), methylbenzophenone (**8**), fluorobenzophenone (**9**), benzophenone (**10**), chlorobenzophenone (**11**) have been analyzed by NMR and GC-MS; the ratio in *ortho/meta/para* isomers have been determined by GC; d) Conversion towards the minor reagent and isolated yield (between brackets) after workup.

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21. ***Bismuth (III) triflate*** . Previous work reported the preparation of $Bi(OTf)_3$, [22] and the crystalline structure of a nonahydrated form has been recently described.[23] We have proposed a new simple and efficient synthesis of this compound from triphenylbismuth and triflic acid.[1] Moreover, thermodynamic studies showed the existence of three hydrated forms $Bi(OTf)_3.nH_2O$, n=9,4,2 between a temperature range from rt to 80°C; the structure of the tetrahydrate (n=4) has been established by X-ray diffractometry.[24] Between 80°C and 100°C, the initiation of decomposition prevents the isolation of pure anhydrous $Bi(OTf)_3$. The catalyst used for the reactions described here was mainly the tetrahydrated form.
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